# CLASSICAL AND QUANTUM DIFFUSION

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## I. Classical Brownian Motion

I have been asked to cover diffusion, more specifically quantum diffusion, and I have two one hour lectures in which to do the impossible. I have, therefore, planned my lectures thus. In Lecture I starting now I will begin by summarizing the physical ideas of classical diffusion and then discuss the underlying Brownian motion - from Einstein-Smoluchowski through Ornstein-Uhlenbeck. In doing so I will be graduating from a highly idealized position - Markoff process, namely the Wiener process, to the physically more admissible phase-space Markoff process, namely the Ornstein-Uhlenbeck process, or in other words, from stochastic kinematics to stochastic dynamics. All this should be quite familiar from the 1943 classic paper of Chandrasekhar [1] in the Reviews of Modern Physics, which remains a standard reference on the physics of the problem to this day. Except, however, that I may emphasize the formal stochastic point of view to a greater extent, in keeping with the theme of this School. The limitation of these idealized stochastic processes when applied to a real many-body problem (e.g. self-diffusion in a liquid, say) will be only very briefly commented upon. Towards the end of the first lecture, I will pose the problem of quantizing the Ornstein - Uhlenbeck process in a certain definite sense. I will also mention a rather interesting related problem of stochastic quantization due to Nelson. Then in Lecture II, I will take up the quantum treatment of the Ornstein-Uhlenbeck process through the Frictional Hamiltonian formalism that incorporates the dissipative effects. I will specifically describe our recent work along these lines that reveals certain inconsistencies of the existing 'exact' treatments and seeks to cure these. While Lecture I is in the nature of an overview, Lecture II is intended as a seminar. For reviews, see refs. [2-6].

### I.1 Diffusion

When we think of diffusion, what immediately comes to the mind is a dust of particles dispersed through and moving chaotically and perpetually in a medium, e.g., historically it was plant pollen in water, but it could be a colloidal suspension, or, for demonstration purposes, carmine in acetone. At the low space-time resolution of a naked human eye, however, one simply observes a material continuum with a coarse-grained number density $n(\vec{x}, t)$ varying slowly in space and time. Furthermore, it is

expected that the natural tendency for the system is to run down in the sense that the spatial gradients of $n(\vec{x}, t)$ are equalized as the system evolves in time implying material transport. (That is assuming the system to be thermodynamically stable, chemically non-reacting and free from active transport). This transport current $\vec{j}(\vec{x},t)$ is described by the empirical Fick's Law

$$\vec{j}(\vec{x},t) = -D \vec{\nabla} n(\vec{x},t) \qquad \text{(I-1a)}$$

for small gradients, defining the diffusion coefficient D. Since the material is locally conserved, one has the continuity equation

$$\frac{\partial n(\vec{x},t)}{\partial t} + \vec{\nabla} \cdot \vec{j}(\vec{x},t) = 0 \qquad \text{(I-1b)}$$

Combining the two one gets the diffusion equation

$$\frac{\partial n(\vec{x},t)}{\partial t} = D \nabla^2 n(\vec{x},t) \qquad \text{(I-1c)}$$

This phenomenological equation, depending on the nature of $n(\vec{x},t)$, forms the basis of the transport theory in numerous contexts of physics, chemistry, biology and astrophysics. I will just mention the historical example of Fourier's treatment of heat conduction in solids. To have a feel for numbers, the self-diffusion coefficient D for most liquids is $\sim 10^{-5}$ cm$^2$ sec$^{-1}$.

Mathematically, (I-1c) is a parabolic differential equation that can be solved for the well posed initial boundary values (i.e. Dirichlet or Neumann conditions and open boundaries) and describes an irreversible evolution into future such that any singularities are smoothed out in the process. The fundamental solution or the propagator $K^o_\infty(\vec{x},t, \vec{x}_o,t_o)$ for an unbounded d-dimensional system is given by

$$K^o_\infty(\vec{x},t;\vec{x}_o,t_o) = \left(\frac{1}{4\pi D(t-t_o)}\right)^{d/2} \exp\left(-|\vec{x}-\vec{x}_o|^2/4D(t-t_o)\right), \quad t \geq t_o \qquad \text{(I-2a)}$$

It corresponds to a delta-function singularity of unit weight concentrated at $\vec{x}_o$ at the initial epoch $t_o$. Thus, the solution for an arbitrary initial distribution $n_o(\vec{x}_o,t_o)$ is given by

$$n(\vec{x},t) = \int n_o(x_o,t_o)\, K^o_\infty(\vec{x},t;\vec{x}_o,t_o)\, dx_o, \quad t \geq t_o \qquad \text{(I-2b)}$$

More generally, for an arbitrary spatial boundary ($\partial\Omega$) condition at t=o, the propagator $K^o_\Omega(\vec{x},t;\vec{x}_o,t_o = o)$ is given by

$$K^o_\Omega(\vec{x},t;\vec{x}_o,t_o = o) = \sum_{n=o}^{\infty} e^{-\lambda_n t} \phi_n(\vec{x})\, \phi_n(\vec{x}_o), \quad t \geq o, \qquad \text{(I-2c)}$$

where $\phi_n$ is the $n^{th}$ eigenfunction associated with (I-1c) and $\lambda_n$ the corresponding eigenvalue for the prescribed boundary condition. Now two generalizations :

a. Diffusion with advection :

The containing medium may itself be in a state of motion described by a velocity field $\vec{v}(\vec{x},t)$ and the diffusing material is assumed to co-move with it. Thus $\partial/\partial t$ in (I-1c) must be replaced by the substantial derivative giving

$$\frac{\partial n}{\partial t} = - \vec{\nabla} . (n \vec{v}) + D \nabla^2 n \qquad \text{(I-3)}$$

A particularly interesting situation is the one in which the velocity-field $\vec{v}(\vec{x},t)$ is turbulent, rendering (I-3) a stochastic differential equation. For $\vec{v}(\vec{x},t)$ a stochastic process stationary to second order with whitenoise spectrum and corresponding to incompressible flow, one obtains enhanced renormalized, diffusion coefficient. Obvious relevance is to diffusion in a system undergoing pre-transitional hydrodynamical instabilities may be noted. This is why the cup of coffee is stirred!

b. Diffusion with drift in a force-field :

Here one assumes that an external force such as the one due to gravity produces a drift velocity analogous to Ohm's law (and not an acceleration). Then, for a force derivable from a potential $V(\vec{x})$

$$\vec{J}(\vec{x},t) = -D \vec{\nabla} n(x,t) - \mu ( \vec{\nabla} V(\vec{x})) \; n(\vec{x},t)$$

$$\frac{\partial n(\vec{x},t)}{\partial t} = D \vec{\nabla} . ( \vec{\nabla} n(\vec{x},t) + \frac{\mu}{D} n(\vec{x},t) \vec{\nabla} V(\vec{x})) \qquad \text{(I-4)}$$

(Smoluchowski equation)

This can be reduced to the previous case by the substitution $n(x,t)=\exp(-\mu V/2D)\, \sigma(x,t)$ that eliminates the term involving $\vec{\nabla}_n . \vec{\nabla} V$ and makes the equation for $\sigma$ self-adjoint. One obtains for the propagator now

$$K_n^V(\vec{x},t;\vec{x}_o,t_o) = \exp ( \mu V(\vec{x}_o)/D) \sum_{n=o}^{\infty} \phi_n(\vec{x}_o) \phi_n(\vec{x}) e^{-\lambda_n t} \qquad \text{(I-5)}$$

where $\phi_n$ is the $n^{th}$ eigenfunction of (I-4) and $\lambda_n$ the corresponding eigenvalue. Note that the Einstein-Nernst relation $\mu/D = 1/k_B T$ obtains on setting $\partial n/\partial t = o$ in (I-4) for equilibrium.

Equation (I-1) - (I-5) describe the macroscopic coarse-grained behaviour observed at the low resolution of a naked eye - 'the harvest of a naked eye'. Now, should we observe the system under the high resolution of an ultramicroscope, as Robert Brown would, the material continuum will resolve into the individual particles in a state of perpetual and chaotic motion - called Brownian motion after the 19th century botanist. We shall not tarry here to look up the rather amusing history of the subject except to note that hardly a century ago this motion was attributed to some form of 'vital' force inherent in the particle, or to some equally obscure 'intestine' motion, and that when finally early this century Einstein, barely aware of Robert Brown's findings, gave the correct quantitative theory, it was only to adduce evidence for the reality of and

the definite finite (non-zero) size for atoms and molecules! His theory was statistical rather than dynamical and that accounted for its success since it circumvented many difficult problems associated with the stochastic differential equations not heard of before Langevin.

I.2 Wiener Process [7,8] :

The correct kinetic theoretic explanation of the Brownian motion is, of course, now well known. The Brownian particle moves under the action of the colliding molecules of the medium which is in a state of thermal agitation - the heat 'bath'. Indeed, recalling that the typical size of a colloidal Brownian particle is $\sim 1\ \mu m$, and there are $\sim 10^{23}$ molecules $cm^{-3}$ in the medium moving at thermal speeds $\sim 10^{5}$ cm $sec^{-1}$, the particle should suffer $\sim 10^{21}$ collisions per second. Given its large inertia $\sim 10^{-12}$ gm it will integrate a large number of small impulses before moving appreciably. Simple appeal to the law of large numbers should make the successive displacements independent, gaussian random variables. The basic ansatz is thus that of 'stosszahl ansatz' or the 'molecular chaos' which is ultimately related to the large number of bath degrees of freedom interacting weakly with the Brownian particle. Thus it is a pedestrian problem. It has to do with the random walk !

Some of the observed general features of the Brownian motion are :

(i) the particles move independently of one another

(ii) successive displacements separated by macroscopic time intervals are statistically uncorrelated

(iii) mean-squared displacement grows linearly with time $t \to \infty$

(iv) the motion is perpetual.

It should be clear from (i) that the normalized density $n(\vec{x},t)$ discussed above may be identified with the probability density of finding the particle at $\vec{x}$ at time $t$, assuming, of course, that the Brownian particles are identical. The question then is what the stochastic motion of the Brownian particle should be in order that the probability density evolves as in (I-1) through (I-5). To answer this question we argue with Einstein that there exists a time scale $\tau$ such that the displacements separated by time intervals $\gg \tau$ are statistically uncorrelated and yet $\tau$ is sufficiently large to ensure large number of collisions before the particle moves appreciably, i.e. $\tau_{macro} \gg \tau \gg \tau_{micro}$. This should certainly be so for large particle inertia, weak coupling to the bath and high temperatures. And now we boldly consider the idealized limit $\tau = o$, This leads us to the following stochastic motion [7] :

$$d\vec{X}(t) = d\vec{W}(t) \quad , \tag{I-6}$$

with $d\vec{W}(t)$ ' s independent, gaussian, white noise, random variables with mean $\langle d W(t) \rangle = o$ and covariance $\langle d W_i(t)\ d W_j(t) \rangle = 2dD\delta_{ij}dt$, and $d\vec{W}(t)$ independent of $\vec{X}(s)$ for $s \leq t$ (the Markoff assumption). Such a position Markoff process is called the Wiener process. The Wiener processes constitutes a classical paradigm in the

sense of Kuhn and forms the kernel of our thinking about all stochastic processes related to diffusion and time dependent statistical mechanics. Its relation to diffusion is rendered more compelling by the following remarkable theorem. Let $p_t(\vec{x})$ be the probability density for the state space $\vec{x}$. Then, given

(a) the Markoffian property (Chapman - Kolmogoroff condition)

$$p_t \otimes p_s = p_{t+s} \quad , \quad o \leqslant t, \quad s \leqslant \infty \quad , \tag{I-7}$$

(b) the persistence - at - a - point, i.e. for $\eta > o$

$$\lim_{t \to o} p_t(\{\vec{x} \mid i\vec{x}| \geqslant \eta\}) = 0(t) \tag{I-8}$$

and

(c) the symmetry $p_t(\vec{x}) = p_t(-\vec{x})$ , for $t > o$, there exists a $D$ such that

$$p_t(\vec{x}) = \left(\frac{1}{4\pi D\, t}\right)^{d/2} \exp\left(-\vec{x}^2/4Dt\right) \quad , \tag{I-9}$$

and

$$\frac{\partial p_t(\vec{x})}{\partial t} = D \nabla^2 p_t(\vec{x}) \quad , \quad t \geqslant o \quad .$$

Probably the most important property of a Wiener process is that the trajectories are continuous but almost nowhere differentiable - the velocities are not defined. In fact the trajectories may not be rectifiable. In modern parlance, these are fractals.

The Wiener process also induces a Wiener measure in the sample space of paths. The latter may be obtained as an n-fold convolution of $p(t,\vec{x})$ in the limit $n \to \infty$ :

$$\lim_{\substack{N \to \infty \\ \Delta t \to o \\ N\Delta t = t}} \left(\frac{1}{4\pi D\, \Delta t}\right)^{\frac{dN}{2}} \exp\left\{-\frac{\Delta t}{4D} \sum_{n=o}^{N} \frac{(\vec{x}_{n+1} - \vec{x}_n)^2}{(\Delta t)^2}\right\} d\vec{x}_1 \ldots\ldots d\vec{x}_N$$

$$\longrightarrow e^{-\frac{1}{4D} \int_{\vec{x}(o)}^{\vec{x}(t)} \left(\frac{d\vec{x}}{dt}\right)^2 dt} \mathfrak{D}[\vec{x}(t)] \tag{I-10}$$

where $\mathfrak{D}[\vec{x}(t)]$ denotes the element of volume in the function space, and we have a functional integration. The connection with the path integral formulation of quantum mechanics is obvious - after all diffusion equation is essentially the Schrödinger equation with imaginary time. This indeed forms the basis of the 'Feynman-Kac' formula that enables one to evaluate the average of the path-dependent quantities [8] :

$$\left\langle \exp\left(-\int_o^t V(\vec{x}(t'))\, dt'\right)\right\rangle = \int K_\infty^V(\vec{x},t;o,o)\, dx \tag{I-11}$$

where $K_\infty^V$ is the propagator for the diffusion equation in a potential, i.e. for

$$\frac{\partial n}{\partial t} = D \nabla^2 n + V(\vec{x})\, n \tag{I-12}$$

A rather interesting example would be to evaluate [9]

$$\langle \exp\,(-\mathcal{U} \mid c_t^a\,(\vec{x}\,(.))\mid)\rangle \quad , \quad \text{where} \quad c_t^a\,(\vec{x}\,(.))$$

is the volume of the Wiener Sausage, i.e.

$$c_t^a\,(\vec{x}(.)) \;=\; U\; S(\vec{y},a) \quad , \quad \vec{y} \in c_t(\vec{x}\,(.)) \quad , \tag{I-13}$$

where $S(\vec{y},a)$ is a sphere of radius a centered at point y $\in$ the image set $c_t(x(.))$ of the path $\vec{x}(s)$, $o \leqslant s \leqslant t$, starting at $\vec{x}(o) = 0$. These spheres may overlap and that is the problem. It turns out that the above can be evaluated to give the remarkable result [9]

$$\lim_{r\to\infty} \frac{1}{t^{d/d+2}} \ln \langle \exp\,(-\mathcal{U} \mid c_t^a\,(x(.))\mid\rangle = -\left(\frac{d+2}{2}\right)\left(\frac{2\gamma_d}{d}\right)^{\frac{d}{d+2}}\mathcal{U}^{\frac{2}{d+2}} \tag{I-14}$$

where $\gamma_d$ is the lowest eigenvalue of $-\frac{1}{2}\nabla_d^2$, with the solution vanishing at the surface of a unit sphere. Physically, the quantity evaluated above may give the survival probability of a particle diffusing in a medium with a uniform distribution of a reactant, a being the 'lethal radius' or the radius of the sphere of influence. Relevance to the Glarum defect - diffusion - relaxation model is obvious.

I.3 Phase-space Markoff - Process and Ornstein-Uhlenbeck Brownian Motion [1,7] :

Brownian motion as described by the Wiener process is a position Markoff process that has a purely stochastic kinematics without any dynamical content. The corresponding diffusion equation is nothing but a rate equation (a master equation). The process is unphysical in that the paths are almost always non-differentiable and hence the velocity undefined. In particular $\langle x^2(t)\rangle \propto t$ on all time scales. For a physical system, the motion must be free (ballistic) and thus $\langle x^2(t)\rangle \propto t^2$ on a sufficiently short time scales. This would make the path differentiable and the velocity well defined. This is demanded by the equipartition law too. Furthermore, the Newtonian dynamics $\vec{F} = m\,\vec{a}$ must be built into it. Thus, one is tempted to replace (I-6) by a phase-space Markoff process

$$\begin{aligned} d\,\vec{x}(t) &= \vec{v}\,(t)\,dt \\ d\,\vec{v}\,(t) &= -\frac{1}{M}\,\vec{\nabla}\,V\,dt + d\,\vec{B}(t) \end{aligned} \tag{I-15}$$

with $\vec{B}(t)$ a Wiener process and $d\,\vec{B}(t)$ independent of $\vec{x}(s)$ and $\vec{v}(s)$ for $s \leqslant t$. This is, however, not quite all right yet. It supposes the stochastic process characterizing the medium (the 'bath') given independently of the test particle, and thus neglects the reaction of the test particle back on the medium. The medium acts but cannot be acted upon ! As can be shows quite trivially (see Lecture II), this would lead to an indefinite acceleration of the particle. Such a stochastic acceleration is, of course,

possible in some cases The Fermi mechanism of stochastic acceleration of cosmic ray particles by 'collisions' with the inhomogeneous magnetic fields frozen - into and co-moving with the material clouds moving at random, is an example in point. Here the particle is hardly expected to affect the motion of these clouds. In general, however the particle will act back on the medium and this reaction will be fed back to the particle with some delay. This would imply a memory for the process B(t) making it non-Markoffian and very hard to calculate. However, for a Brownian particle of large inertia diffusing through a dense medium of lighter (mass m) particles, the situation is not quite so bad. For instance, there must be a Doppler Friction inasmuch as there are more collisions head on (a priori !) than from behind (a posteriori !). The reaction may be simulated by an instantaneous dynamical viscous drag $-\gamma \vec{v}$ , treating $d\vec{B}(t)$ as the residual 'bath' force. Thus one gets [7]

$$d\vec{x}(t) = \vec{v}(t)\, dt$$

$$d\vec{v}(t) = -\gamma \vec{v}(t)\, dt - \frac{1}{M} \vec{\nabla} V + d\vec{B}(t) \quad , \qquad \text{(I-16)}$$

where the Wiener process $\vec{B}(t)$ has now $\langle dB(t)^2 \rangle = 2d(\gamma k_B T/M)\, dt$ to ensure eventually (as $t \to \infty$ ) equipartition law (thermalization). This is the stochastic Langevin equation describing the Ornstein-Uhlenbeck process. It gives $\langle x^2(t) \rangle \propto 2dDt$ for $t \gg \gamma^{-1}$ but $\langle x^2(t) \rangle \propto t^2$ for $t \ll \gamma^{-1}$. Here $D = (k_B T)/m\gamma$ . Modern theory of Brownian motion is based on this. It is readily seen, that in the limit of large friction $\gamma$ , one recovers the position Markoff process discussed earlier.

It must be re-emphasized that when the inertia of the Brownian particle (M) is comparable to that of the bath particles (m) (e.g. in the problem of self-diffusion) the memory effects are important. In fact the test particle sets up a vortex - like back flow so that the momentum imparted to the medium head on is returned to the test particle from the rear in the 'antiperistaltic' fashion. This, for instance, makes the velocity-velocity correlation function $\langle v(o)\, v(t) \rangle$ start out analytically with zero slope at t=o and fall off asymptotically slower than the exponential - indeed algebraically as $t^{-d/2}$. Such long Non-Debye tails have been seen in molecular dynamical calculations [10] . The Ornstein-Uhlenbeck process on the other hand predicts an exponential correlation $e^{-\gamma|t|}$ which is non-analytic at t=o. There is in fact an inconsistency [5] due to the assumption that dB(t) is independent of $\vec{x}(s)$ and $\vec{v}(s)$ for $s \leqslant t$, which must break down as $s \to t$. In order to incorporate the Non-Markoffian (memory) effects, one must consider a fully dynamical treatment such as the one due to Zwanzig [11] and Mori [12] . One can recover [13] the Markoffian Langevin equation perturbatively as $(m/M) \to 0$. The conditions under which the system can act as its own bath were examined by Ford, Kac and Mazur (FKM) [14] . Non-Markoffian effects are particularly important for thermally activated escape over barriers [15] .

The Ornstein-Uhlenbeck process will form the basis for our quantum treatment in Lecture II. By quantization what is implied is treating the deterministic part of the Hamiltonian including frictional term quantum mechanically. The stochastic driving

process is still to be treated classically.

A technical remark now. The various stochastic processes discussed above and the corresponding equations for the probability densities $p(\vec{x},t)$ generated by them are related very generally as follows [6] . For a system of stochastic differential equations

$$\dot{x}_\nu = f_\nu(\vec{x}, t; \omega), \quad \nu = 1,2,.....n, \tag{I-17}$$

with $\omega$ the random variable or function, one can write down the Liouville equation for the phase-space density

$$\frac{\partial \rho}{\partial t} = -\sum_\nu \frac{\partial}{\partial x_\nu} (\rho \ f_\nu) \tag{I-18}$$

Then it is readily shown that

$$p(\vec{x},t) = \langle \rho(\vec{x},t) \rangle_\omega \tag{I-19}$$

While performing ensemble averages $\langle \ldots \rangle_\omega$ of functionals $F[\omega(t)]$ over the gaussian random variables $\omega(t)$, the following identity due to Novikov [16] comes in very handy

$$\langle \omega_i(t) \ F[\vec{\omega}(t)] \rangle_\omega = \sum_j \int dt' \ \langle \omega_i(t) \ \omega_j(t') \rangle_\omega \ \cdot$$

$$\cdot \left\langle \frac{\delta F[\vec{\omega}(t)]}{\delta \omega_j(t') \ \delta t'} \right\rangle_\omega \tag{I-20}$$

When the random variable is delta-correlated, i.e. it has white noise, it enables one to close the hierarchy of coupled equations. Thus (I-18) leads to the associated Fokker-Planck equation in general.

And finally a brief excursion into stochastic quantization of Nelson [7] . The original physical motivation namely that of providing a 'hidden variable' classical substratum to quantum mechanics is of no concern to us here. We are only concerned with the mathematical aspect. The essential point is that for all measurements reducible to position measurements, any state of the system described by the Schrödinger equation

$$i\hbar \frac{\partial \phi}{\partial t} = -\frac{\hbar^2}{2M} \nabla^2 \phi + V(\vec{x},t)\phi \tag{I-21}$$

is equivalent to a position Markoff process

$$d\vec{x}(t) = -\vec{b}(\vec{x}(t), t) \, dt + d\vec{W}(t) \quad , \tag{I-22}$$

with $\vec{W}(t)$ a Wiener process ($\vec{W}(t) - \vec{W}(s)$ independent of $\vec{W}(r)$ for $r \leqslant s \leqslant t$) having a diffusion coefficient = $\hbar/2m$. The drift (forward) velocity $\vec{b}(\vec{x}(t), t)$ is given by $\vec{b} = \vec{v}$ (current velocity) + $\vec{u}$ (osmotic velocity), where

$$\frac{\partial \vec{u}}{\partial t} = -\frac{\hbar}{2M}\vec{\nabla}(\vec{\nabla}\cdot\vec{v}) - \vec{\nabla}(\vec{u}\cdot\vec{v})$$

$$\frac{\partial \vec{v}}{\partial t} = -\frac{1}{M}\vec{\nabla}V - (\vec{v}\cdot\vec{\nabla})\vec{v} + (\vec{u}\cdot\vec{\nabla})\vec{u} + \frac{h}{2M}\vec{\nabla}^2\vec{u} \qquad \text{(I-23)}$$

Thus the velocity-field equations are to be solved subject to the given initial conditions (Cauchy data) $\vec{u}_o(x)$ and $\vec{v}_o(x)$ that can be related to the given initial state through

$$\phi = e^{R+iS}, \quad \frac{m\vec{v}}{\hbar} = \vec{\nabla}S, \quad \frac{m}{\hbar}\vec{u} = \vec{\nabla}R \qquad \text{(I-24)}$$

The probability density $\rho = |\phi|^2$ satisfies the (forward) Fokker-Planck equation

$$\frac{\partial \rho}{\partial t} = -\vec{\nabla}\cdot(\rho\vec{b}) + \nu\nabla^2\rho, \quad \nu = \frac{\hbar}{2M} \qquad \text{(I-25)}$$

generated by (I-22).

In this description one combines the kinematics of Wiener process with the dynamics (force-acceleration relation) of the Ornstein-Uhlenbeck process sans dissipation. All I want to emphasize now is that for $V(\vec{x},t)$ a random variable, $\vec{b}(\vec{x}(t), t)$ will be a stochastic process and hence equation (I-25) should lead to a renormalized diffusion constant as discussed earlier [3] . Thus the problem of a quantum particle moving in a time-random potential reduces to that of a classical diffusion in a turbulent medium. In point of fact stochastic quantization may enable one to treat at once intrinsic quantum mechanical probability along with the classical randomness (of thermal origin).

We will end with a general remark. Ultimately, diffusion refers to time dependent randomness, i.e. randomness may be taken to reside in the particle itself (like the Mexican jumping beans). This must be distinguished from the case where the randomness lies in the medium (spatial). The latter is a much more difficult (percolation) problem and can lead to localization. Ultimately, this difficulty may be attributed to our inability to define meaningfully a Markoff process for multi-dimensional 'time'.

## II. Quantum Diffusion

The Ornstein-Uhlenbeck process is perhaps the simplest stochastic process that is a physically admissible idealization and has a non-trivial domain of validity. It has intuitive appeal and forms the basis of modern theory of Brownian motion. It approximates the time-dependent statistical mechanics of a many-body system where one identifies the few, relatively slow hydrodynamical degrees of freedom of interest, widely separated on time-scale from the almostly infinitely many, fast microscopic degrees of freedom, the details of which are of no interest to us, and that collectively form the thermal 'bath'. It thus provides a generalized hydrodynamics in which the hydrodynomical degrees of freedom with long auto-correlation times obey macroscopic

equations of motion driven parametrically by the 'noise' terms having short auto-correlation time, representing the influence of the 'bath' forces, whose statistical properties are assumed simple and given. The reaction of the hydrodynamical degrees of freedom back on the bath is thus ignored except in some average sense, e.g., through the dynamical friction ($-\beta\vec{v}$) term in the Langevin equation. I must hasten to add that while such a 'back action evasion' may be justified by intuitive appeal to large inertia, weak coupling to bath and to the large number of 'bath' degrees of freedom, the intuition is at times belied by explicit microscopic calculations possible for some simple nonlinear systems.

With these remarks, we now turn to the problem of quantization of the 'Brownian motion a la Langevin'. We have in mind a particle (electron, say) weakly coupled to the 'bath' (thermal phonons). At not too low a temperature, the auto-correlation time for the phonon displacement field is sufficiently short compared to the electron velocity auto-correlation time to justify the assumptions of Langevin. By quantization here we mean treating the electron motion quantum mechanically, but treating the bath force still as a given stochastic process. It is tempting therefore to consider as the quantum analogue a particle moving in a time-random potential, as indeed has been done by several workers [17-21] . The existing theoretical treatments are based almost entirely on the lattice (L) Hamiltonian, namely the tight-binding one-band Hamiltonian [19]

$$H_L = \sum_i E_i(t) \mid i \rangle\langle i \mid + \sum_{i \neq j} V_{ij}(t) \mid i \rangle\langle j \mid \quad , \qquad \text{(II-1)}$$

in obvious notation. The dynamical disorder is introduced by treating the potentials, i.e., the site-diagonal and the off-diagonal matrix elements, as random c-number variables, evolving stochastically in time. Such a time dependence is known to arise from the random modulation of the potential by the incoherent lattice vibrations of thermal origin. It must be emphasized here that in all the treatments referred to above, as also in the treatment to follow, this time dependence is taken to be parametric in that the potential is supposed to introduce no additional dynamical degrees of freedom in the problem. For the Gaussian choice of randomness having a white-noise spectrum, i.e., $\delta$ -correlated in time but arbitrarily correlated in space, the problem has been solved exactly by several workers [17-21] . In all cases one obtains a classical diffusive behavior in that the mean square displacement $\langle x^2(t) \rangle \sim t$, for $t \to \infty$, implying a well defined diffusion constant and hence mobility. This common result, however plausible and expected from the physical point of view, is surprising when analyzed more carefully. Indeed, as the following exact treatment [22] reveals, for the corresponding continuum problem we have $\langle x^2(t) \rangle \sim t^3$ asymptotically, implying nondiffusive motion. Thus, the diffusive behavior obtained by the other workers is due presumably to the specific nature of the one-band lattice Hamiltonian.

In order to appreciate this point fully it is expedient to consider first the related problem of classical diffusion a la Langevin equation in a spatial one-dimen-

sional continuum :

$$m \; du/dt \; = \; - \; \Gamma u + f(t) \; , \qquad \text{(II-2)}$$

where the fluctuating random force f(t) and the concomitant dissipation represented by the frictional coefficient are related by the fluctuation-dissipation theorem, i.e.,

$$< f(t) \; f(t') > \; = 2k_B T \Gamma \; \delta(t-t') \; \equiv \; \Delta^2 \; \delta(t-t') \; .$$

As is well known this gives a mean square displacement $< x^2(t) > \sim 2Dt$, for $t \gg m\Gamma^{-1}$, defining the diffusion constant $D = k_B T/\Gamma$ . If, however, we omit the dissipative term ($- \Gamma u$) from Eq.(II-2), i.e., we set

$$m \; du/dt = f(t) \; , \qquad \text{(II-3)}$$

we can readily show that

$$< x^2(t) > \sim ( \Delta^2/4m^2) t^3, \quad \text{for } t \to \infty \quad . \qquad \text{(II-4)}$$

This implies a nondiffusive random motion. Here the particle continues to absorb energy from the fluctuating force and accelerates indefinitely. In short the particle 'heats up' to an infinite temperature. Now, the quantum mechanical treatment based on the Hamiltonian $H_L$ in (II-1) corresponds precisely to this nondissipative classical system in that no dissipation is incorporated explicitly in $H_L$. And yet the mean - square displacement calculated exactly from (II-1) shows a diffusive behavior as noted above. In the following, we address ourselves to this paradoxical situation. More specifically, we will first show that the exactly solvable continuum analog of (II-1) also reproduces $t^3$ behavior as in (II-4). We then argue that the diffusive behavior obtained by other workers referred to above is entirely due to the one-band lattice nature of the Hamiltonian given in (II-1). And finally we will present a proper treatment of quantum diffusion including friction.

To this end we will now obtain an exact solution of the quantum problem in a continuum. For simplicity we shall treat the case of one space dimension. Generalization to arbitrary dimension is straightforward. The quantum evolution is now given by the time-dependent Schrodinger equation,

$$i\hbar \; \frac{\partial \psi}{\partial t} \; = \; - \frac{\hbar^2}{2M} \; \frac{\partial^2 \psi}{\partial x^2} \; + \; V(\vec{x},t) \, \psi \quad , \qquad \text{(II-5)}$$

where $V(\vec{x},t)$ is the stochastic potential assumed to be Gaussian, with space-time correlation

$$< V(x,t) \; V(x',t') > \; = \; V_o^2 \; \delta(t-t') \quad g(x-x') \qquad \text{(II-6)}$$

The physical quantities of interest can be conveniently expressed in terms of the reduced density matrix $\rho(x',x,t)$ where

$$\rho(x',x,t) \quad \equiv \quad \psi^*(x',t) \; \psi(x,t) \quad , \qquad \text{(II-7)}$$

and the angular brackets denote the average over the stochastic potential. Clearly

$\rho(x', x,t)$ is a functional of the Gaussian random variable $V(x,t)$ and hence the Novikov theorem applies. Following essentially the earlier treatments, we get the equation of motion

$$\frac{\partial}{\partial t}\langle \rho(x',x,t)\rangle = -\frac{i\hbar}{2M}\left(\frac{\partial^2}{\partial x^2} - \frac{\partial^2}{\partial x'^2}\right)\langle \rho(x', x,t)\rangle - \frac{V_o^2}{\hbar^2}\left[g(o) - g(x-x')\right]\langle\rho(x,x',t)\rangle \qquad \text{(II-8)}$$

This has to be solved subject to the initial condition that the particle was prepared initially in a wave packet centered at the origin, x=o. We shall take conveniently

$$\rho(\vec{x}', x,t=o) = \psi^*(x',t=o)\ \psi(x,t=o),$$

where

$$\psi(x,t=o) = ((2\pi)^{\frac{1}{4}}\sigma^{\frac{1}{2}})^{-1}\ \exp\left(-x^2/4\sigma^2\right) \qquad \text{(II-9)}$$

This ensures correct normalization. Here $\sigma$ denotes the spatial spread of the initial wave packet. Because of the unbounded nature of the kinetic energy operator in the continuum limit, it is necessary to choose a wave packet with $\sigma > 0$. The asymptotic ($t \to \infty$) behavior is, of course, independent of the precise form of the wave packet. This problem does not arise in the case of the lattice Hamiltonian $H_L$ which is bounded. Equation (II-8) can be solved by first taking the time Laplace transform and then considering the resulting hyperbolic equation in the two independent variables x and x'. We get

$$\frac{2i\hbar}{M}\frac{\partial^2}{\partial x\,\partial y}\ \tilde{R}(X,Y,s) + \left(s + \frac{V_o^2}{\hbar^2}\ g(o) - \frac{V_o^2}{\hbar^2}\,g(y)\right)\tilde{R}(X,Y,s) = R(X,Y,t=o), \qquad \text{(II-10)}$$

where we have introduced the characteristic coordinates $X = x + x'$, $Y = x - x'$. Here s is the Laplace transform variable. We have defined

$$R(X,Y,t) \equiv \rho(x',x,t)\ ;\ \tilde{R}(X,Y,s) = \int_o^\infty R(X,Y,t)\ e^{-st}\,dt \qquad \text{(II-11)}$$

This mean square displacement can be expressed as

$$\langle x^2(t)\rangle = \frac{1}{8}\ \frac{\partial^2}{\partial K^2}\ \bar{\tilde{R}}(K,y=o,t)\ \Big|_{K=o}\ , \qquad \text{(II-12)}$$

with

$$\bar{\tilde{R}}(K,y,t) = \int_{-\infty}^{\infty} R(X,Y,t)\ e^{iKx}\,dx\ . \qquad \text{(II-13)}$$

Here an overbar denotes the spatial Fourier transform while a tilde denotes the time Laplace transform. Equation (II-12) holds provided $\bar{R}(K,Y=O,t)$ is analytic in K at K=O.

Equation (II-10) can be converted into an ordinary differential equation in Y by taking Fourier transform with respect to X, which can then be solved readily subject to the initial condition to give

$$\tilde{\bar{R}}\ (K,Y{=}0,s) = \int_0^\infty 2\ \exp\left[-(2\sigma^2 + \frac{\hbar^2 y^2}{2M^2\sigma^2})\ K^2\right] e^{-sy}$$

$$\exp\left\{-\frac{V_o^2}{\hbar^2}\left[g(o)\ y - \int_o^y g\ (\frac{2\hbar\,|K|\,'}{M})\ dy'\right]\right\}\ dy \qquad \text{(II-14)}$$

The right-hand side of this equation is already in the form of a Laplace transform. Hence we get at once on inversion

$$\bar{R}\ (K,Y{=}o,t) = 2\ \exp\left[-\left(2\sigma^2 + \frac{\hbar^2 t^2}{2M^2\sigma^2}\right)\ K^2\right]$$

$$\exp\left\{-\frac{V_o^2}{\hbar^2}\left[g(o)\ t - \int_o^t g\ (\frac{2\hbar\,|K|\,y'}{M})\ dy'\right]\right\} \qquad \text{(II-15)}$$

One can confirm that (II-15) fulfills the normalization and the initial condition. We now choose an explicit form for the function g(Y). For simplicity we take it to be Gaussian, i.e.,

$$g(Y) = \left[(2\pi)^{\frac{1}{2}}\alpha\right]^{-1} \exp\ (-y^2/2\alpha^2) \qquad \text{(II-16)}$$

With this choice, $\bar{R}(K,Y{=}0,t)$ can be seen to be analytic in K at K=0. Thus from (II-12), (II-15) we get for the mean-square displacement

$$\langle X^2(t)\rangle = \sigma^2 + \frac{\hbar^2}{4M^2\sigma^2}\ t^2 + \frac{1}{3\sqrt{2\pi}}\ \frac{V_o^2}{M^2\alpha^3}\ t^3 \qquad \text{(II-17)}$$

This is an exact result. It shows clearly that the particle motion is nondiffusive on any time scale. In fact, the above result is quite general and depends only on the fact that g(Y) is an even function of Y and is analytic in Y at Y=0. The special case $g(Y) \sim e^{-\alpha|y|}$ which is not analytic at Y=0 calls for a somewhat more detailed evaluation by quadrature. Thus, we confirm that the quantum motion in a fluctuating continuum gives nondiffusive motion. The result is essentially identical to that for the classical motion in a fluctuating medium as in (II-3) and (II-4). In point of fact one may choose V(x,t) = xf(t) such that the random force obtained as the gradient of potential V(x,t) is actually f(t) as in (II-3). One can readily verify that the asymptotic time behavior remains cubic as obtained above.

The fact that the exact quantum treatment on the lattice gives diffusive behavior has, therefore, to do with the specific nature of the lattice Hamiltonian $H_L$. The question is how to understand this difference. The point is that a one-band lattice Hamiltonian has a momentum cutoff inherent in it. This limiting momentum is related to the Bragg reflection at the Brillouin zone boundary or, what is essentially the same, one has the Umklapp process. The lattice acts as an infinite momentum sink and prevents indefinite acceleration of the particle. More transparently, as the particle quasimomentum increases towards the limiting value, the group velocity decreases and even reverses sign. Since it is the group velocity that leads to physical displacement the above results are understandable.

In order to see more clearly how such a limiting momentum can lead to diffusive motion, it is very revealing to consider again the classical motion in a fluctuating medium described by (II-3), with the proviso that the physical velocity u be defined modulo some limiting velocity $u_o$, say. This mathematically simulates the umklapp process. For instance, we could redefine physical velocity as

$$v = u_o \sin (2\pi u/u_o) \qquad \text{(II-18)}$$

and calculate the mean square displacement, with v as the physical velocity. We get

$$\langle x^2(t) \rangle = \langle \{ \int_o^t u_o \sin [ 2\pi \int_o^{t'} f(t'')\, dt'' ]\, dt' \}^2 \rangle \ ,$$

$$= u_o^2\, a\, (t + 2a\, e^{-t/a} - \frac{1}{2}\, a\, e^{-2t/a} - \frac{3}{2}\, a) \ , \qquad \text{(II-19)}$$

where $a = u_o^2 / 2\pi^2 \Delta^2 M^2$ . It is clear that

$$\langle x^2(t) \rangle \sim u_o^2\, a\, t \qquad \text{as } t \to \infty \ , \qquad \text{(II-20)}$$

which is again diffusive. In deriving this we have used the well-known result $\langle \exp [ i \int_o^t f(t')dt' ] \rangle = \exp [ - (\frac{1}{2} \Delta^2) t ]$ . It seems clear, therefore, that the quantum treatment based on the lattice Hamiltonian is <u>per se</u> not a quantum analog of the Brownian motion. The diffusive behavior with $H_L$ results entirely from the momentum absorption by the lattice via Bragg reflections. The latter is absent in the case of the continuum, and hence the nondiffusive behavior.

Finally, we must clarify that for a quantum particle in a real fluctuating continuum, we do expect a diffusive behavior. Here the effect of the interaction of the test particle with the dynamical degrees of freedom of the background fluctuating medium, however, cannot be represented entirely by a stochastic potential V(x,t) having a parametric time dependence. We must necessarily incorporate the analog of a dissipative term as well. In the following, quantum diffusion in dynamically disordered medium is reformulated treating explicitly the friction concomitant with the randomly fluctuating potential. The correct diffusive behaviour, namely $\langle x^2(t) \rangle \sim t$ is obtained both in the lattice as well in the continuum limit. This cures the unphysical $\langle x^2(t) \rangle \sim t^3$ behaviour inherent in the existing treatments, resulting from the neglect of friction as noted above. I will take for simplicity the spatial dimensionality to be unity, but as can been seen readily from the treatment, there is no loss of generality on this count.

As the neglect of frictional effects shows up rather dramatically in the continuum case, we shall consider this case first. Since quantum mechanics subsumes a classical Lagrangian, we are led to considering the classical limit first. Here the situation is familiar. The motion of the particle acted upon by the stochastic bath forces of thermal orgin is known to be an Ornstein-Uhlenbeck process described well by the Langevin equation

$$\frac{d^2x}{dt^2} = -\gamma\frac{dx}{dt} - \frac{1}{M}\frac{\partial V}{\partial X} + \frac{1}{M} f(t) \quad , \tag{II-21a}$$

with

$$\langle f(t)\ f(t')\rangle = 2\gamma M k_B T\ f_o^2\ \delta(t-t') \tag{II-21b}$$

Equation (II-21b) related explicitly the friction coefficient $\gamma$ to the random force f(t), assumed to be Gaussian and delta-correlated. Here V(x) is a given static potential. The dissipative Lagrangian $L_D$ associated with (II-21) is now readily constructed following the approach due originally to Helmholtz [23] . For example, if

$$G = \ddot{q} + g(q,\dot{q},t) \approx 0 \tag{II-22}$$

is the given equation, then there exists an 'integrating factor' $f(q,\dot{q},t)$ and an effective Lagrangian $L^*(q,\dot{q},t)$ such that

$$f\,G = \frac{d}{dt}\frac{\partial L^*}{\partial \dot{q}} - \frac{\partial L^*}{\partial q} \quad , \tag{II-23}$$

where f is given by the solution of

$$g\frac{\partial \ell nf}{\partial \dot{q}} + \frac{\partial g}{\partial \dot{q}} = \frac{\partial \ell nf}{\partial q}\dot{q} + \frac{\partial f}{\partial t} \tag{II-24}$$

Thus one can solve for $L^*$. Since fG = 0 implies G = 0 ( for $f \neq 0$) $L^*$ is the Lagrangian sought for. In the present case one readily obtains

$$L_D^* = e^{\gamma t}\left[\frac{1}{2} M\dot{x}^2 - V(x) + xf(t)\right] \tag{II-25}$$

Defining the canonical momentum $p = \partial L_D^* / \partial \dot{x} = m\dot{x}\ e^{\gamma t}$ , one gets the associated Hamiltonian

$$H_D^* = \dot{x}\,p - L = e^{-\gamma t}\frac{1}{2M} p^2 - e^{\gamma t} f(t)\,x + e^{\gamma t} V(x) \tag{II-26}$$

This is the well known frictional Hamiltonian and has been used extensively in other contexts, e.g. frictional effects in nuclear reactions [23-25] . In the following we will drop superscript star.

Now, for the quantum treatment we can proceed via the path-integral formulation using the Lagrangian $L_D$ (as we will do in the continuum case), or via the canonical quantization of $H_D$ (as we will do for the lattice case). Thus, we will be illustrating both approaches without being repetitive.

In order to calculate the mean-squared displacement $\langle x^2(t)\rangle$ , let the particle be prepared initially in a gaussian wave-packet centered at origin i.e.,

$$\psi(x,t=o) = \left(\frac{1}{\sqrt{2\pi}\sigma}\right)^{\frac{1}{2}} \exp\left(-x^2/4\sigma^2\right) \tag{II.27}$$

We then have

$$\langle x^2(t)\rangle = \left\langle \int_{-\infty}^{\infty} x^2\ \psi^*(x,t)\ \psi(x,t)\ dx \right\rangle \quad , \tag{II-28}$$

where the time developed $\psi(x,t)$ can be related to the initial state $\psi(x,t=o)$ by

the propagator $K_D(x,t', x',t')$ as

$$\psi(x,t) = \int_{-\infty}^{\infty} K_D(x,t, x',o)\ \psi(x',o)\ dx' \qquad t \geqslant o \qquad \text{(II-29)}$$

Here the angular bracket denotes average over f(t).

Finding $K_D(k,t; x',t')$ corresponding to $L_D$ (with V(x)=O for the present case) is highly non-trivial because of the exponential ($e^{-\gamma t}$) prefactor that complicates the associated measure, or the normalization. Fortunately, this problem has been solved for the arbitrary bilinear Lagrangian by Papadopoulos [26]. Specializing his results to the present case, we get after some straightforward quadrature

$$\langle x^2(t)\rangle = \sigma^2 + \frac{\hbar^2}{M^2\sigma^2\gamma^2}\ \sinh^2\left(\frac{\gamma t}{2}\right)\ e^{-\gamma t} +$$

$$+ \frac{2k_BT}{M}\ e^{-\gamma t}\left[t\, e^{\gamma t} + e^{-\gamma t}\ (e^{2\gamma t} - 1)\ \frac{1}{2\gamma} - \frac{2}{\gamma}\ (e^{\gamma t} - 1)\right]$$

$$\simeq \left(\frac{2k_BT}{M\gamma}\right) t\ , \qquad \text{for} \quad t \gg \frac{1}{\gamma}\ . \qquad \text{(II-30)}$$

This implies diffusive behaviour. One readily verifies, that neglecting friction, i.e., setting $\gamma \simeq 0$, recovers the unphysical behaviour

$$\langle x^2(t)\rangle \sim t^3\ , \quad \text{for} \quad \frac{M\sigma^2}{\hbar} \ll t \ll \frac{1}{\gamma} \qquad \text{(II-31)}$$

Identical results are obtained if we calculated using the frictional Hamiltonian $H_D$ instead.

We will now consider the case of the lattice Hamiltonian in the one-band tight-binding limit, considered in most existing treatments sans friction. Taking cue from the form of $H_D$ in (II-26), one is tempted to consider a lattice Hamiltonian with the off-diagonal (kinetic) matrix elements having the factor $e^{-\gamma t}$, and the diagonal (potential) matrix elements having the factor $e^{+\gamma t}$, apart from being random. As we shall presently see this turns out to be incorrect.

In the case of the lattice, the potential V(x)=V(x+a), where 'a' is the period. The quantum Hamiltonian $H_D$ must be re-written in the representation in which the basis functions are the complete orthonormal set of Wannier functions $\chi_m^\alpha(x)$ corresponding to the non-random Hamiltonian $\hat{p}^2/2m + V(x)$ :

$$\sum_{\alpha,m} \chi_m^{\alpha *}(x)\ \chi_m^{\alpha}(x') = \delta(x-x')\ ,$$

$$\int_{-\infty}^{\infty} \chi_m^{\alpha *}(x)\ \chi_n^{\beta}(x)\, dx = \delta_{\alpha\beta}\delta_{mn}\ , \qquad \text{(II-32)}$$

where $\alpha$ is the band index and m labels the sites. Now, to project out the one-band Hamiltonian one has only to retain the matrix elements diagonal in the band index. We then have

$$H_{DL} = \sum_{m,\Delta} e^{\gamma t} V_o \mid m \rangle\langle m+\Delta \mid + f(t)\, a\, e^{\gamma t} \sum m \mid m \rangle\langle m \mid, \quad \text{(II-33)}$$

where $\Delta$ spans nearest neighbours. Here we have kept only the dominant matrix elements, e.g. $e^{\gamma t} + e^{-\gamma t} \simeq e^{\gamma t}$ since we will be interested in the limit $\gamma t >> 1$. I must hasten to add that none of these simplifying approximations are essential to what follows. $H_{DL}$ is the simplest lattice Hamiltonian incorporating dissipation. Both diagonal as well as off-diagonal terms carry the factor $e^{\gamma t}$. It is not at all obvious that the exponentially growing non-random off-diagonal terms will be off-set by the exponentially growing random diagonal terms to give a diffusive behaviour for long times. But this is precisely what happens as will be shown in the following.

We will now calculate $\langle x^2(t) \rangle$. Let the particle be prepared at the original site m = o at t = o. It is convenient to introduce a reduced density matrix $\langle \rho_{mn}(t) \rangle = \langle a_m^*(t)\, a_n(t) \rangle$, where $a_m$ is the wave amplitude at site m. The initial condition is $\langle \rho_{mn}(t=o) \rangle = \delta_{m,o}\, \delta_{n,o}$. The equation of motion for $\langle \rho_{mn}(t) \rangle$ is readily found to be

$$i\hbar \frac{\partial \tilde{\rho}_{p,q}(\tau)}{\partial \tau} = \frac{4V_o}{(2\gamma\tau)^{\frac{1}{2}}} \cdot \tilde{\rho}_{p,q}(\tau) \sin p \sin (q/2) - \left(\frac{f_o^2 a^2}{2 i \hbar}\right) \cdot \frac{\partial^2 \tilde{\rho}_{p,q}(\tau)}{\partial p^2}, \quad \text{(II-34)}$$

where we have introduced the lattice Fourier transform

$$\langle \tilde{\rho}_{p,q} \rangle = \sum_{m,n} \langle \rho_{mn}(t) \rangle\, e^{ikm - ik'n} \quad \text{(II-35)}$$

with

$$p + \tfrac{1}{2} q = k, \quad p - \tfrac{1}{2} q = k', \text{ and } e^{2\gamma t} = \tau .$$

Thus all summations over p,q span first Brillouin zone. As before, we have used the Novikov identity for functionals of gaussian random variables to close the hierarchy of equations. As we are interested only in some moments, e.g., $\langle x^2(t) \rangle$, it is not necessary to solve (II-34) for $\tilde{\rho}_{p,q}(\tau)$. We simply have to expand both sides of (II-34) in powers of q and equate coefficients of like powers. The first three equations are

$$\dot{\tilde{\rho}}_{p,o}(\tau) = D_o \frac{\partial^2 \tilde{\rho}_{p,o}(\tau)}{\partial p^2}, \quad \text{(II-36)}$$

$$\dot{\tilde{\rho}}'_{p,o}(\tau) = \left(\frac{2\gamma}{i\hbar\sqrt{2}\gamma}\right) \frac{1}{\tau^{\frac{1}{2}}} \tilde{\rho}_{p,o}(\tau) \sin p + D_o \frac{\partial^2 \tilde{\rho}'_{p,o}(\tau)}{\partial p^2} \quad \text{(II-37)}$$

$$\dot{\tilde{\rho}}''_{p,o}(\tau) = \left(\frac{4\gamma}{i\hbar\sqrt{2\gamma}}\right) \frac{1}{\tau^{1/2}} \tilde{\rho}'_{p,o}(\tau) \sin p + D_o \frac{\partial^2 \tilde{\rho}''_{p,o}(\tau)}{\partial p^2} \,, \tag{II-38}$$

with $D_o = a^2 f^2/2\hbar^2$, prime denoting $\partial/\partial q$, and overhead dot denoting $\partial/\partial\tau$. The mean-squared displacement, or rather the diffusion constant D, if it exists, can be expressed as

$$D = \lim_{t\to\infty} \frac{1}{2} \frac{d}{dt} \langle x^2(t) \rangle = \lim_{\tau\to\infty} -\left(\frac{\gamma a^2 \tau}{\pi}\right) \int_{-\pi}^{\pi} \dot{\tilde{\rho}}''_{p,o}(\tau)\, dp$$

$$= \lim_{\tau\to\infty} -\left(\frac{2V_o}{i\hbar\pi}\right) (2\gamma\tau)^{1/2} \int_{-\pi}^{\pi} \tilde{\rho}'_{p,o}(\tau) \sin p\, dp \tag{II-39}$$

In getting the last equality, we have made use of (II-38) and the periodic boundary condition in p so that the contribution of the last term in (II-38) vanishes identically. All we have to do now as to solve (II-36) for $\tilde{\rho}_{p,o}(\tau)$, substitute the solution in (II-37) as the inhomogeneous term and solve for $\tilde{\rho}'_{p,o}(\tau)$, and finaly substitute this solution in (II-39). Since the equations are of the parabolic type, one simply needs the Green function $G(p, \tau; p', \tau')$ subject to the periodic boundary condition. This is readily found to be

$$G(p, \tau; p', \tau') = \sum_{n=-\infty}^{\infty} \frac{1}{\left[4\pi D_o(\tau - \tau')\right]^{1/2}} e^{-\frac{((p-p')-2\pi n)^2}{4 D_o (\tau - \tau')}} \tag{II-40}$$

Thus, the diffusion constant turns out to be

$$D = \lim_{\tau\to\infty} \left(\frac{8 V_o^2 a^2}{4\pi\hbar^2}\right) \int_{1}^{\tau} e^{-D_o(\tau - \tau')} \left(\frac{\tau}{\tau'}\right)^{1/2} d\tau'$$

$$= \frac{2 V_o^2}{\pi M \gamma k_B T} \tag{II-41}$$

This would correspond to a temperature - dependent mobility. This expression is similar to but not quite the same as the one we would obtain in the conventional treatment of dynamic disorder for a lattice Hamiltonian with site-diagonal disorder.

Let me now put this work in the proper perspective. We considered the quantum motion of a particle (subsystem) under the influence of its interaction with the rest of the system (bath). If the bath is taken to act on the particle parametrically as a c - number stochastic force, we get non-diffusive motion i.e. indefinite acceleration. (The fact that for a one-band lattice Hamiltonian one got diffusive behaviour is due to the momentum cut off inherent in such a model). We attributed this unphysical motion to the neglect of friction concomitant with the fluctuating stochastic force. We then introduced friction through the phenomenological frictional Hamiltonian and recovered the physical, diffusive motion. But, now we must ask if the frictional Hami-

ltonian (II-26) is consistent with quantum mechanics, vis - a - vis the fact that $[\hat{x}, \hat{p}_{kin}] = i\hbar e^{-\gamma t} \longrightarrow 0$ as $t \longrightarrow \infty$, implying violation of the uncertainty principle. This is concerned with the basic problem of treating dissipation in quantum mechanics that has a long history of non-success starting from the introduction of the frictional Hamiltonian almost half a century ago by Bateman [27] and Kanai [28] through the classic work of Ford-Kac-Mazur (FKM) [14]. Comprehensive reviews have appeared since then [24,25]. Very briefly, just that the Lagrangian (II-25) gives the correct classical equation of motion (i.e. the Langevin equation (II-21)) does not imply that it also gives a unique and correct quantum mechanics. Indeed, it has been claimed that only a coordinate dependent dissipative potential is consistent with quantum mechanics [29]. One must note, however, that $[\hat{x}, \hat{p}_{kin}] = i\hbar e^{-\gamma t}$ by itself may not imply violation of $\Delta x \, \Delta p_{kin} \geq \hbar/2$. We must evaluate the uncertainty product in the time-evolved wavefunction. For the case of damped harmonic oscillator, and most studies are limited this case, it has been possible in some sense to preserve the uncertainty principle [24]. More recently, however, the violation for certain initial states and certain specific time instants has been reaffirmed [30]. In fact, it has been shown that the Schrödinger and the Heisenberg pictures of the evolution consistent with equilibration as $t \longrightarrow \infty$ do not exist for the frictional Hamiltonian. It seems that the effect of the bath dynamical degrees of freedom may not be representable entirely by a c - number white noise stochastic force [31]. In point of fact the FKM treatment of the quantum Langevin equation requires a quantized gaussian noise, with non-zero correlation time $\hbar/k_B T$ for the case of coupled Harmonic oscillators. Thus, the status of the frictional Hamiltonian is far from secure. We must add, however, that in the present case of a freely diffusive particle, one can explicitly show that the uncertainty product $\Delta x \, \Delta p_{kin} \geq \hbar/2$ for all times (and the quantum statistical expectation of the frictional Hamiltonian goes over to $1/2\, k_B T$ as $t \rightarrow \infty$). But, of course, one must show that the inequality holds with probability unity and not just on the average. This is under investigation.

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